IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re the Application of: Group Art Unit: 1793

GERARD LASLAZ et al   Examiner: J. Morillo

Serial No.: 10/560,819

Filed: December 15, 2005

For: MOULDED Al-Si-Cu ALUMINIUM ALLOY COMPONENT
      WITH HIGH HOT-PROCESS RESISTANCE

DECLARATION UNDER 37 CFR 1.132

Honorable Commissioner for Patents
PO Box 1450
Alexandria, VA 22313-1450
Sir:

I, Michel Garat, do hereby declare as follows:

I am a named inventor of the above-identified patent application.

I graduated in 1973 as an Engineer from the Ecole de Physique et de Chimie Industrielles de la Ville de Paris. I also obtained a DEA in Polymers in 1973.

I joined the Centre de Recherche in Voreppe, France in 1974 and spent my entire career employed by Aluminium Pechiney (subsequently owned by Alcan and Rio Tinto). I have always worked in the field of Foundry Alloys, either in research or in development, and I am at present Project Manager, R&D Foundry Alloys in the Primary Metal Group in Voreppe.

In this declaration, I will discuss the effect of vanadium on creep resistance in aluminum alloys, and the effect of interaction between V and Ti and B on grain refinement in aluminum alloys.

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1. Effect of vanadium on creep resistance

I am responsible for testing to determine the effect vanadium content on creep strength of aluminum alloys.

Creep occurs when an alloy is subjected to a relatively low level of stress (significantly lower to the tensile Yield Stress) at high temperature for a relatively long time (typically 50 to 1000 hrs). The mechanism of deformation and subsequent rupture is totally different from that of the conventional tensile test at the same temperature, which is carried out in at most a few minutes. Basically, in the case of creep, everything else being equal, the lower the deformation, the higher the creep strength.

Four variables are related in creep behavior: temperature, stress, time and resulting deformation. Consequently, several methods of creep strength measurement exist.

The results described in Tables 1 and 2 appended hereto were obtained by two different methods:

- In Table 1, the stresses designated $\sigma 0.1/100$ were compared. $\sigma 0.1/100$ is the stress that leads to a 0.1% deformation after 100 hrs at a temperature of 300°C. To determine this value, cylindrical creep test-pieces of the TR1-1 type (Dia. 4 mm) were tested at 300°C at different stresses for a time of 100 hrs and the deformation of each test piece is recorded. By interpolation, the stress that leads to 0.1% deformation was determined. The higher the stress, the better the creep strength.

More specifically, the set of experiments summarized in Table 1 were carried out on alloys substantially free of magnesium (< 0.01%). The $\sigma 0.1/100$ of AlSi5Cu3.75MnZrTi alloys with 0.27% vanadium and without vanadium were determined, with two heat treatments, a standard T7 heat treatment and an improved T7* heat treatment made possible by the low magnesium

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content. A 9% increase of σ0.1/100 was observed with the standard T7 and a 10% increase with the improved T7*, compared with the alloy without vanadium.

- In Table 2, the method used was to apply a constant stress to all samples (which were the same TR1-1 testpieces), this stress being on the order of magnitude of the above described σ0.1/100 for the considered type of alloy, here 30 MPa at 300°C, and to allow the creep test to continue for at least 300 hrs. Deformation vs. time is continuously recorded, and deformations at 100, 150, 200 and 300 hrs are plotted and compared.

The experiments summarized in Table 2 were carried out on alloys similar to those of Table 1, but containing 7% silicon instead of 5% and the maximum level of Mg (0.10%) of the claimed invention.

The deformation of the alloy without vanadium is already much higher than that of the 0.17% and 0.21% V alloys after 150 hrs, and alloy without vanadium breaks before 200 hrs with deformation of the order of 2.4 to 4%; the alloy containing vanadium resist breakage at least for 300 hrs with deformations of 0.4 - 0.9%.

These two sets of experiments clearly demonstrate the improvement of creep strength brought about by vanadium addition.

2) Interaction between V and Ti and B on grain refinement.

Vanadium, like several peritectic elements, is by itself a potential grain refiner because it forms Al3V compounds onto which the alpha-aluminum crystals can nucleate.

However, the most effective and at present almost universal method of grain refinement of the alpha-aluminum phase is to add a combination of titanium and boron, resulting in formation of TiB_2, which is the most effective nucleant of

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alpha-aluminum.

In wrought alloys of the 2xxx, 3xxx, 5xxx, 7xxx series
with do not contain silicon, only a small amount of Ti (of the
order of a few hundred ppm) is needed, combined with boron,
with a Ti/B ratio of the order of 2 to 5. In Al-Si
hypoeutectic foundry alloys of the 3xxx series typically
containing between 5 and 11% by weight silicon, a much greater
amount of Ti is needed, as part of the Ti is combined with Si
in Al-Ti-Si compounds. Usual amounts of Ti in such alloys are
0.03-0.25% by weight, and preferably 0.10-0.15%. To this
initial amount of Ti incorporated in the alloy, refiners such
as AlTi5B1 are added in a proportion of typically 0.05% to
0.2% by weight in order to create TiB_2 nuclei.

If vanadium is present, part of the boron is entrapped in
chemically stable VB_2 compounds whose grain refinement ability
is much inferior to that of TiB_2 or even nil. Consequently,
the grain refinement obtained at given Ti and B levels is
lower than in a similar alloy which does not contain vanadium.
This effect is exemplified in the concurrently filed
declaration of Stéphane Vernède, which shows that in a 3104
alloy, the addition of 200 to 400 ppm of V causes an increase
in grain size.

In above-identified patent application, the addition of
vanadium is motivated by its strong favorable effect on creep
strength and the grain coarsening effect is accepted, and can
be mitigated by a higher TiB_2 addition. Moreover, the grain
size is not necessarily critical in a cylinder head, as the
secondary dendrite arms spacing, solely controlled by the
solidification rate, is by far the most important structural
parameter.

I hereby declare that all statements made herein of my
own knowledge are true and that all statements made on
information and belief are believed to be true, and further

that these statements were made with the knowledge that
willful false statements and the like so made are punishable
by fine or imprisonment, or both, under 18 U.S.C. 1001 and
that such willful false statements may jeopardize the validity
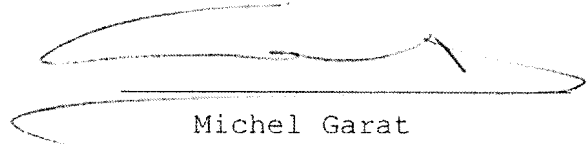of the application or any patent issued thereon.

7 January 2002
Date

Michel Garat

Table 1

	Si	Fe	Cu	Mn	Mg	Zr	V	Ti	Creep strength at 300°C	
									T7 σ 0.1/100 (MPa)	T7* σ 0.1/100 (MPa)
Reference alloy	5,00	0,10	3,75	0,10	< 0,01	0,13	0,00	0,13	26,6	28,8
Alloy according to the invention	5,00	0,10	3,75	0,10	< 0,01	0,13	0,27	0,13	29,0	31,8
Analytical precision +/-	0,30	0,02	0,15	0,02		0,02	0,03	0,02	Effect of V on creep strength	
									+ 9%	+ 10%

Cast testpieces : The alloys were cast as AFNOR Dia. 18 mm permanent mold testbars, which were later machined to the dimensions of the creep testpiece

Heat treatments : T7 : conventional solutionizing 495°C - 10 hrs + Water Quench + aging 210°C - 4 hrs
T7* : high temperature solutionizing 515°C - 10 hrs + Water Quench + aging 210°C - 4 hrs

Creep strength : σ 0.1/100 is the stress that causes a deformation of 0.1% after a 100 hours at the considered temperature

Table 2

Alloy	Mg %	V %	E-0h	E-100 h	E-100h Mean	E-150h	E-150h Mean	E-200h	E-200h Mean	E-300h	E-300h Mean
A	0,10	0	0	0,8		3,3		Rupture at 156h, E =3.8%			
	"	"	0	0,5	0,53	1,3	1,80	Rupture at 175h, E = 2.4%			
	"	"	0	0,3		0,80		Rupture at 185h, E = 4%			
B	0,10	0,17	0	0,17		0,26		0,40		0,88	
	"	"	0	0,15	0,15	0,22	0,22	0,30	0,31	0,59	0,60
	"	"	0	0,12		0,17		0,22		0,33	
C	0,10	0,21	0	0,14		0,22		0,32		0,58	
	"	"	0	0,14	0,13	0,21	0,20	0,31	0,30	0,58	0,54
	"	"	0	0,12		0,18		0,26		0,45	

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